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⑯ Production of three-dimensional objects.

⑯ A method for producing three-dimensional objects having distinctly coloured elements or elements having a distinct tactile characteristic ; as described. The objects, for example anatomical models can be prepared by stereolithography. In one such technique a film of a photohardenable composition containing a photoresponsive agent is provided. The film is irradiated in a cross-sectional pattern of the object to be formed. One or more portions of the cross-sectional pattern corresponding to the selected elements are selectively irradiated to activate the photoresponsive agent. The steps are repeated to form successive adjacent cross-sectional patterns of the object and these patterns are integrated to provide the object.

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The invention relates to the preparation of three-dimensional models from tomographic or CAD/CAM data wherein the models include one or more elements or portions which have a distinct colour from other elements or portions in the model or which have a distinct texture, resilience or other tactile characteristic from other elements in the model.

Several methods and apparatus have been developed for the production of three-dimensional objects or models by irradiation of compositions which crosslink and solidify upon irradiation. U.S. Patents 4,041,476 and 4,228,861 to Swainson describe the formation of three-dimensional objects by solidifying each point individually by scanning a volume point by point with intersecting beams of radiation. The Swainson methods are complex and expensive.

U.S. Patent 4,575,330 to Hull describes a method for preparing three-dimensional objects by building up successive thin layers of a solidified photopolymerizable composition. This method has become known as stereolithography. In one embodiment described in the Hull patent, a three-dimensional object is constructed by establishing a thin layer of a photocurable composition on the surface of a platform immersed in a bath of the composition and scanning the layer with a laser beam. The laser controls the X, Y dimension of the model. The Z dimension is controlled by incrementally lowering the platform to greater and greater depths after each successive layer corresponding to a cross-section of the model is polymerized or crosslinked.

Another method for producing three-dimensional objects is described in U.S. Patent 4,940,412 to Blumenthal which discloses a method in which hard copy images having transparent and opaque portions are used as a mask in a photographic process to produce layers which are subsequently stacked and attached to produce a three-dimensional object.

Models prepared previously by the foregoing process methods have been essentially homogeneous in colour and texture. The present inventors have now found a way to prepare models in which selected elements can be distinctly coloured or endowed with a distinct texture, resilience or other tactile characteristic.

In accordance with a first aspect of the present invention that there is provided a method for producing a three-dimensional object having selected elements which are coloured differently from other elements of said object, comprising the steps of:

- a. providing a film of a photohardenable composition containing a photoresponsive agent,
- b. irradiating said film in a cross-sectional pattern of the object to be formed,
- c. selectively irradiating one or more portions of said cross-sectional pattern corresponding to said selected elements which are desired to be coloured differently with radiation which acti-

vates said photoresponsive agent, said photoresponsive agent thereby producing colour in or removing colour from said selected irradiated portions of said cross-sectional pattern,

- 5 d. repeating said steps a, b and c to form successive adjacent cross-sectional patterns of said object, and
- e. integrating said cross-sectional patterns together to provide said object.

In a second and alternative aspect of the invention, there is provided a method for producing a three-dimensional object having selected elements which are coloured differently from other elements of said object, comprising the steps of:

- 10 a. providing a film of a photohardenable composition,
- b. irradiating said film in a cross-sectional pattern of the object to be formed,
- c. depositing a dye on one or more portions of said cross-sectional pattern corresponding to said selected elements which are desired to be coloured differently,
- 20 d. repeating said steps a, b and c to form successive adjacent cross-sectional patterns of said object, and
- e. integrating said cross-sectional patterns together to provide said object, or after said step b said step c being performed before.

According to a third alternative aspect thereof, the invention provides a method for producing a three-dimensional object having selected elements which have tactile characteristics different from those of other elements of said object, the method comprising the steps of:

- 35 a. providing a film of a photohardenable composition containing a photoresponsive agent capable of altering tactile characteristics,
- b. irradiating said film in a cross-sectional pattern of the object to be formed,
- c. selectively irradiating one or more portions of said cross-sectional pattern corresponding to said selected elements in which a different tactile characteristic is desired with radiation which activates said photoresponsive agent and thereby altering the tactile characteristic of said selected portions,
- 40 d. repeating said steps a, b and c to form successive adjacent cross-sectional patterns of said object, and
- e. integrating said cross-sectional patterns together to provide said object.

Thus it will be seen that three-dimensional objects having distinctly coloured elements or elements having a distinct tactile characteristic can now readily be prepared. In preferred arrangements, the three-dimensional objects are prepared by stereolithography.

In one embodiment, photoresponsive agents are

incorporated into the photohardenable composition. As each lamina of the object is formed, the lamina is scanned with radiation which selectively addresses the photoresponsive agent to cause the agent to bleach, colourize, or alter the tactile characteristic of a portion of the model. Scanning to alter the colour or tactile characteristic can be conducted before, during or after the exposure which forms the lamina.

In another embodiment, a combination of photo-bleachable photoinitiators is used to harden the photohardenable layer. The radiation which is used to harden a preselected portion of the model is selected based upon the colour which is desired in that portion of the model. That is, by selecting a radiation which bleaches one of the photoinitiators in the photohardenable composition, the photohardenable composition will be hardened by radicals or other reactive species generated by the bleached photoinitiator while the unbleached photoinitiator colors the layer in the hardened area. In other portions of the model in which another color is desired, the photohardenable layer is hardened by exposure to radiation which bleaches another of the photoinitiators causing it to harden the layer while the remaining photoinitiator(s) color the layer.

In another embodiment, substantially colorless color formers are microencapsulated in a photodecomposable composition or they are incorporated into a photosoftenable composition and formed into microparticles. These agents are incorporated into the photohardenable composition. After or simultaneously with irradiation of the photohardenable layer, the microcapsules or microparticles are selectively irradiated at a distinct wavelength to cause them to decompose, rupture or otherwise release the contained color former. The color former reacts with the photopolymer or other agents in the composition to color the color former and hence color a portion of the model.

In still another embodiment ink jet or similar techniques are used to selectively deposit reactive or non-reactive dyes in those portions of a cross-sectional layer in which color is desired such that the dye becomes reacted into or entrapped within the layer as the layer is hardened.

The term "tactile characteristic" is used herein to mean texture, resilience, elasticity, hardness, etc.

The term "element" is used herein to mean any portion of a model such as a tumor within a model of a brain or a ligament within a model of a knee.

The term "X-Y layer" refers to a single cross-section or lamina of a three dimensional object which is individually scanned or otherwise irradiated and stacked to form a three-dimensional object.

While the invention will be particularly described with respect to its use in conjunction with stereolithography, those skilled in the art will appreciate that the teachings herein can also be used to modify other

processes for producing three-dimensional objects such as those described in the aforementioned patent to Blumenthal.

Our methods will also be described with reference to processes in which the color-determinative or tactile characteristic determinative irradiation step is conducted after the cross-sectional pattern is exposed. Those skilled in the art will appreciate that the former step may be conducted before, after or simultaneously with the latter step

In accordance with one embodiment a photochromic material is incorporated into the photohardenable composition. The photochromic material may be a photobleachable dye or a colorless dye which is colored by exposure to radiation. After scanning each X-Y layer to harden it, the layer may be scanned or otherwise irradiated to color selected areas of the layer and, hence, selected elements of the three-dimensional object when the X-Y layers are stacked. In stereolithographic processes, the layers are stacked automatically as the platform is lowered in the Z-dimension. In the Blumenthal process, the layers are stacked mechanically. In the case of a photohardenable composition containing a photobleachable dye, the X-Y layer is subsequently exposed in those selected areas in which color is not desired. In the case of a photocolorable agent, those areas of the X-Y layer in which color is desired are subsequently exposed. The photochromic agent cannot respond to the radiation which is used to harden the X-Y layer. Otherwise, the agent will be colored or bleached as the layer is hardened. Accordingly, a photochromic material is selected which is sensitive at wavelengths which are distinct from the wavelength of radiation used to harden the X-Y layer. In this manner, by subsequently irradiating those portions of the X-Y layer in which color is desired or not desired, colored elements can be formed in the three dimensional object.

Examples of photobleachable dyes useful in the aforementioned method are well known *per se* and include merocyanine transformations of the benzospirobopyrans described in U.S. Application Serial No. 07/649,100 filed February 1, 1991.

The aforementioned photochromic agents will be used in amounts which impart the desired color density to the model. A typical photohardenable composition may contain about .02 to 1 parts of the photochromic dye per 100 parts monomer.

Examples of photocolorable dyes useful in the aforementioned methods are also well known include the benzospirobopyrans described in U.S. Application Serial No. 07/649,100 filed February 1, 1991.

Another embodiment utilizes diazo chemistry. A photocurable X-Y layer containing a monomer, a diazo compound and a photoinitiator is irradiated with visible light to harden it in those areas corresponding to the solid areas of the three-dimensional object. Af-

ter each X-Y layer is formed, those portions of the X-Y layer in which color is not desired are irradiated with ultraviolet radiation. The X-Y layer is then treated with ammonia vapor analogous to treatments used in blue-printing to selectively color the unirradiated areas.

Diazo compounds useful in this example of the method are well known per se and include those compounds used in conventional blue printing. The ammonia gas treatment can be carried out by conducting irradiation in a chamber which can be flooded with ammonia gas following exposure.

In another arrangement, microcapsules or microparticles containing colour formers or colour precursors are prepared. The walls of the microcapsules may be formed from a photodecomposable wall-forming polymer as described in Japanese patent publication 52-34488 (September 3, 1977). Alternatively, photosoftenable microparticles may be formed from photosoftenable compositions as described in U.S. Patent 4,788,125; or the color former may be microencapsulated with a photodecomposable agent that ruptures the microcapsule wall as described in Japanese Publication 44-17733 (August 4, 1969). By incorporating the color former into a photosensitive microcapsule or a photosensitive microparticle as described in the aforementioned references, a color former which would otherwise not be photoresponsive is rendered photoresponsive. By exposing the microcapsule or microparticle to actinic radiation after hardening the X-Y layer, the wall of the capsule or the particle decomposes and the color former is released. As in the case of the photochromic agents, the sensitivity of the microcapsules or microparticles must be distinct from that of the photohardenable composition such that the color precursor can be selectively released independent of the hardening of the X-Y layer.

In a more specific embodiment, the photohardenable composition may contain multiple sets of microcapsules or microparticles which individually contain different color formers. For example, three sets of microcapsules or microparticles respectively containing cyan, magenta and yellow color formers may be used to produce models having elements individually colored any number of different colors or which may be colored an authentic color. For example, microcapsules or microparticles can be prepared which will decompose or soften upon exposure to distinct bands of radiation. After hardening the X-Y layer, the cyan, magenta and yellow microcapsules or microparticles can be selectively exposed to distinct bands of radiation in selected areas of the X-Y layer in order to produce a desired color in a desired portion of the X-Y layer. For example, in those portions of the X-Y layer which are within elements in which a yellow color is desired, the layer would be exposed to radiation which decomposes the yellow color former-containing microcapsules or microparticles. This portion of

the X-Y layer would not be exposed to radiation which decomposes the cyan-containing or magenta-containing microcapsules or microparticles. At the same time, in those areas of the X-Y layer corresponding to elements in which red is desired, the layer would be exposed to radiation which decomposes the magenta-containing and yellow-containing microcapsules or microparticles without exposing those areas to radiation which decomposes the cyan-containing microcapsules or microparticles.

Color formers are essentially colorless compounds. Typically they are colored by reaction with an acid or a base. Accordingly, to color the color former released from the microcapsule or microparticle, an acid or basic compound must be incorporated in the photohardenable composition. Alternatively, where the polymer formed is acid or basic, it by function as a developer for the color former.

Useful examples of color formers are well known per se and can be found in U.S. Patent 4,399,209.

In another arrangement, the photohardenable composition contains a combination of two or more photobleachable initiators. In this arrangement, the X-Y layer can be selectively coloured by subtracting out colour from the layer as the X-Y layer is formed. In this case, the X-Y layer is not uniformly exposed to the same wavelength of radiation in order to harden it. Rather, each portion of the layer is exposed to a wavelength selected based upon the colour which is desired in that particular portion of the X-Y layer. In one manifestation of this, a combination of cyan, magenta and yellow photobleachable initiators is used. These photoinitiators bleach as they initiate polymerization. In one class of photobleachable initiators, polymerization is initiated by a reductive electron transfer (Chesneau and Neckers, *J. Photochem.*, 42, 269 (1988)) which produces the initiating radical intermediate and, in the process, the photoinitiators lose their colour.

A subtractive color separation model for the formation of a three-dimensional object in authentic color is thus possible. A monomer mixture containing cyan, magenta and yellow photoinitiator dyes which bleach as they form photopolymer is prepared. Their absorptions must be carefully matched such that they can be individually activated and bleached. Initiation is triggered by radiation tuned to the respective cyan, magenta or yellow absorbing wavelength. Computer input controls the wavelength, power and duration of the irradiation step to thereby control not only the formation of the X-Y layer but also the color of each portion thereof. For example, if initiation is triggered by the yellow absorbing

Examples of other reactive dyes which can be used include any dye which is modified to include a vinyl group. Examples of non-reactive dyes are readily available in the art.

From the standpoint of producing selective colo-

ration, the composition of the photohardenable composition is not particularly critical. Examples of monomers, oligomers, and photoinitiators useful in photohardenable compositions are described in European publication No. 0 393 672 to DuPont and U.S. patent 4,575,330, to Hull.

In a further arrangement, tactile characteristics of selected portions of the three-dimensional model are modified. In this arrangement, the degree of crosslinking is increased in selected areas of the X-Y layer to produce a tactile difference. One of the principal applications is in the preparation of three-dimensional anatomical models; it would be desirable in preparing these models to alter the tactile characteristics of certain portions of the model so as to mimic the difference touch, texture or resilience of various anatomical features. For example, in preparing a model of the knee, it would be desirable to form the bone of a highly crosslinked essentially inelastic polymer and to form the ligaments from a more elastic polymer.

One technique for imparting different tactile characteristics to the model is to irradiate the X-Y layer to produce a first level of crosslinking in the polymer forming the layer. Subsequently, additional crosslinking can be introduced into selected portions of the layer by additional exposure. Alternatively, differences in the degree of crosslinking which result in different tactile characteristics may be produced by modulating the intensity of the laser beam as the X-Y layer is scanned.

One possible chemistry for use in achieving tactile differences through adjusting degree of crosslinking is based on oxime acrylates and is described in detail in Kumar, G.S., and Neckers, D.C., "Laser-induced Three Dimensional Photopolymerization Using Visible Initiators and UV Cross-Linking by Photosensitive Monomers *Macromolecules* Vol. 24, No. 15, p 4322 (1991). Oxime acrylates have absorption maxima in the UV range. The paper describes a study of photopolymerization of oxime acrylates with visible initiators using an argon ion laser and photocrosslinking of pendant groups using He-Cd UV laser or a high pressure mercury vapor lamp. Thus, the X-Y layer in this embodiment may be polymerized by scanning with a visible light laser and a second scan with a UV laser can be used to modify the degree of crosslinking and to produce a tactile difference.

## Claims

1. A method for producing a three-dimensional object having selected elements which are coloured differently from other elements of said object, comprising the steps of:
  - a. providing a film of a photohardenable composition containing a photoresponsive agent,

5. b. irradiating said film in a cross-sectional pattern of the object to be formed,
10. c. selectively irradiating one or more portions of said cross-sectional pattern corresponding to said selected elements which are desired to be coloured differently with radiation which activates said photoresponsive agent, said photoresponsive agent thereby producing colour in or removing colour from said selected irradiated portions of said cross-sectional pattern,
15. d. repeating said steps a, b and c to form successive adjacent cross-sectional patterns of said object, and
20. e. integrating said cross-sectional patterns together to provide said object.
2. A method according to Claim 1, wherein said photoresponsive agent is a photobleachable dye.
25. 3. A method according to Claim 1, wherein said photoresponsive agent is a colour precursor microencapsulated in a photodecomposable wall forming polymer.
30. 4. A method according to Claim 1, wherein said photoresponsive agent is a photosoftenable microparticle containing a colour precursor.
35. 5. A method according to any preceding claim, wherein said photohardenable composition contains a plurality of photoresponsive agents, each agent controlling the formation of a different colour such that selected portions of said objects may be coloured differently.
40. 6. A method according to any preceding claim, wherein said step c is performed after said step b.
45. 7. A method according to any of Claims 1 to 6, wherein said step c is performed simultaneously with step b.
50. 8. A method according to Claim 7, wherein said photoresponsive agent is a photobleachable photoinitiator.
55. 9. A method for producing a three-dimensional object having selected elements which are coloured differently from other elements of said object, comprising the steps of:
  - a. providing a film of a photohardenable composition,
  - b. irradiating said film in a cross-sectional pattern of the object to be formed,
  - c. depositing a dye on one or more portions of said cross-sectional pattern corresponding to

said selected elements which are desired to be coloured differently,  
d. repeating said steps a, b and c to form successive adjacent cross-sectional patterns of said object, and  
e. integrating said cross-sectional patterns together to provide said object,  
said step b said step c being performed before said step c..

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10. A method according to Claim 9, wherein a dye is capable of reacting with said photohardenable composition to thereby immobilize said dye in said photohardenable composition.

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11. A method for producing a three-dimensional object having selected elements which have tactile characteristic: different from those of other elements of said object, the method comprising the steps of:

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a. providing a film of a photohardenable composition containing a photoresponsive agent capable of altering tactile characteristics,  
b. irradiating said film in a cross-sectional pattern of the object to be formed,  
c. selectively irradiating one or more portions of said cross-sectional pattern corresponding to said selected elements in which a different tactile characteristic is desired with radiation which activates said photoresponsive agent and thereby altering the tactile characteristic of said selected portions,  
d. repeating said steps a, b and c to form successive adjacent cross-sectional patterns of said object, and  
e. integrating said cross-sectional patterns together to provide said object.

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## EUROPEAN SEARCH REPORT

Application Number

EP 92 30 9025

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A,D	EP-A-0 171 069 (UVP) * claims *	1-11	G03C9/08 G03F7/105
A	WO-A-9 010 254 (BOWLING GREEN STATE UNIVERSITY) * page 26, line 25 - line 38 * * page 30, line 6 - line 11 *	1-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C G03F B29C
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	07 JANUARY 1993	DUPART J-M.B.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			